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DIFFUSION OF SILVER IN ITS OXIDES

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ABSTRACT. Silver oxide specimens containing control amounts of radioactive silver-110 isotope were annealed in contact with silver oxide specimens without the radioactive isotope to determine the diffusion of silver in silver peroxide in the temperature range from 20 to 85°C and in silver oxide in temperature range from 20 to 163°C. In

these ranges the diffusion coefficient varies from 10^{-16} to 10^{-13} cm².sec⁻¹ for silver in silver peroxide and from 10^{-12} to 10^{-10} cm².sec⁻¹ for silver in silver oxide. Equations are presented showing the variation in the diffusion coefficients as a function of temperature.

The silver electrode which is used in silver-zinc electrochemical current sources represents a system consisting of a metal and its oxides where the oxidation-reduction processes, the rate of oxide layers growth and the migration of silver (or of oxygen) in them have not been completely studied to date. Data from investigation of diffusion in the pertinent materials play a major role in the evaluation of these processes. In particular, under definite conditions (for example when processes take place in the solid phase), the diffusion of silver in the oxides may characterize the oxidation reaction rate for silver electrodes.

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There are no data in the literature on the diffusion of silver in oxides. There are experimental data on diffusion in oxides of other metals with analogous chemical and structure properties. The closest of such oxides are copper oxides. Diffusion in cupric oxide was investigated in ref. 1 by means of the copper-64 radioactive isotope. The method of removing a thin layer was used to determine the diffusion coefficient of copper. The distribution of copper diffused over the thickness of test specimens was investigated by considering variation in the relative specific activity of successively removed layers.

The present work is concerned with the investigation of silver diffusion in cuprous oxide in the temperature range 20-160°C and in cupric oxide in the temperature range 20-85°C by means of the silver-110 radioactive isotope.

Experimental Part

The diffusion coefficients were determined using the method of ref. 2, 3 to investigate diffusion in oxides. Specimens were pressed from the test

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material and from the same material containing a control amount of the corresponding radioactive isotope. The two types of specimens were placed in contact under pressure and were annealed at the given temperature which caused the penetration of the radioactive isotope into the specimen which was free of it at the start. After annealing the radioactivity of the test specimen was measured. Compared with the method of the active thin layer which is also frequently used in the study of diffusion, this method has the advantage that it is not necessary to remove thin layers and it yields results which are more reproducible. The computations of the diffusion coefficient in this case are very simple because we are dealing with a quasi-infinite diffusion system consisting of two specimens which are in contact.

The general equation for the case of quasi-infinite domains has the form (ref. 4)

$$M = qc_0 \sqrt{D\tau} \left\{ \int_0^{\infty} [1 - \Phi(a)] da \right\}.$$

The integral in the right side is equal to $\sqrt{\pi}$. From this we obtain

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$$D = \frac{M^2 \pi}{q^2 c_0^2 \tau}; \text{ cm} \cdot \text{sec}^{-1}$$

where D is the diffusion coefficient in $\text{cm}^2 \cdot \text{sec}^{-1}$, M is the amount of the diffused radioactive tracer in counts/min, q is the contact surface of the specimens in cm^2 , c_0 is the initial activity in counts/min·cm³, τ is the diffusion annealing time.

The above equation was used to compute the coefficients of diffusion in the present work.

The test specimens were prepared in the following manner. Specimens of the test material were prepared in the form of pellets with a weight of 2.5 grams from peroxide and oxide powders at a pressure of 120 kg/cm²; specimens containing the silver-110 radioactive isotope had the form of a silver plate which was plated electrochemically with a layer of radioactive silver whose thickness was from 0.0114 to 0.1760 cm and whose relative activity was up to 132,000 counts/min.

The test sample was placed in contact with the radioactive layer of the silver plate, using a pressure of 10 kg/cm² in a special sleeve. In this form it was placed into a thermostat for annealing. After annealing specimen was separated from the plate, dissolved in nitric acid after which its activity was determined in counts/min.

In the case of silver oxide the specimens in contact with the radioactive layer were annealed at a temperature of 20 to 165°C while in the case of silver

peroxide the annealing temperature was from 20 to 85°C. The relatively low annealing temperature is necessary due to the low dissociation temperatures for silver oxides (200°C for the oxide and 90°C for the peroxide).

At 20°C the specimens were held for 150 days in the case of silver oxide and for 312 days in the case of silver peroxide. At higher temperatures the specimens from silver oxide were thermostatically controlled for 4 to 5 hours while in the case of silver peroxide they were controlled for 15 to 30 hours.

The results of the measurements are shown in the table.

Figures 1 and 2 which use semi-logarithmic coordinates show the variation in the coefficient of diffusion as a function of temperature. The figures have been used to determine the values of the activation energy and the term in front of the exponent in the equation for the diffusion coefficient.

For silver peroxide $D_0 = 1.96 \times 10^2 \text{ cm}^2 \cdot \text{sec}^{-1}$, $Q = 25,000 \text{ cal/mole}$, while for silver oxide $D_0 = 5.4 \times 10^{-8} \text{ cm}^2 \cdot \text{sec}^{-1}$, $Q = 6960 \text{ cal/r e}$.

We can see from the results that silver in the oxide and peroxide has substantially different diffusion coefficients which apparently is associated with the diffusion mechanism.

In developing the diffusion mechanism in Ag_2O it is convenient to make the following comparisons. In silver oxide Ag_2O the maximum value of the

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TABLE. MEASUREMENTS TAKEN AFTER ANNEALING SILVER PEROXIDE AND SILVER OXIDE AT DIFFERENT TEMPERATURES

| Annealing Temperature (°C) | Annealing Time (hr) | Activity of specimen containing silver-110 isotope (counts/min) | Activity of the diffused silver-110 isotope (counts/min) | Diffusion Coefficient (cm ² /sec) |
|----------------------------|---------------------|---|--|--|
| <u>Silver peroxide</u> | | | | |
| 20 | 3650 | 46200 | 11800 | $0.74 \cdot 10^{-12}$ |
| 85 | 3,7 | 16070 | 108 | $0.61 \cdot 10^{-11}$ |
| 100 | 5,0 | 6210 | 244 | $0.90 \cdot 10^{-11}$ |
| 140 | 4,0 | 16870 | 770 | $0.186 \cdot 10^{-10}$ |
| 163 | 4,0 | 6530 | 320 | $0.32 \cdot 10^{-10}$ |
| <u>Silver Oxide</u> | | | | |
| 20 | 5800 | 104000 | 27 | $2.42 \cdot 10^{-18}$ |
| 52 | 30 | 13200 | 47 | $2.31 \cdot 10^{-14}$ |
| 55 | 29,2 | 5800 | 28 | $2.92 \cdot 10^{-14}$ |
| 58 | 20,8 | 13150 | 37 | $3.33 \cdot 10^{-14}$ |
| 85 | 29,3 | 13070 | 224 | $5.4 \cdot 10^{-13}$ |

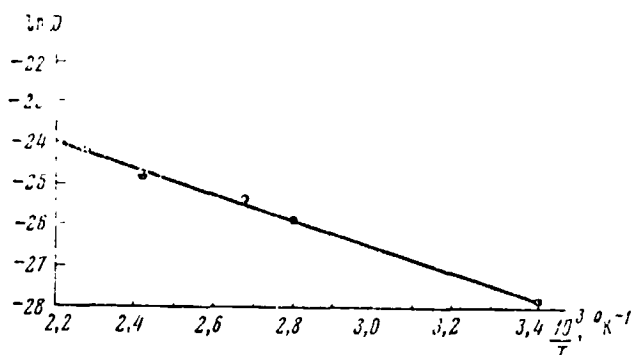


Figure 1. Variation in the diffusion coefficient of Ag in Ag_2O as a function of temperature

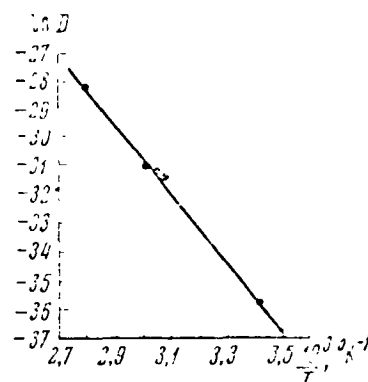


Figure 2. Variation in the diffusion coefficient of Ag in AgO as a function of temperature

diffusion coefficient for silver reaches a value of $10^{-10} \text{ cm}^2 \cdot \text{sec}^{-1}$ temperature of 165°C (close to the temperature of dissociation).

In its order of magnitude it is very close to that of the diffusion coefficient for copper in cuprous oxide Cu_2O (maximum value up to $2.8 \times 10^{-10} \text{ cm}^2 \cdot \text{sec}^{-1}$).

The closeness in the values of the diffusion coefficients is apparently due to the closeness in the chemical and structural properties of these oxides.

The ionic radii of Cu^+ and Ag^+ differ little and are 0.98 \AA and 1.13 \AA respectively. The crystalline lattice type is the same--it is cubic. The nature of the chemical bond is also the same--it is ionic. The energies of the crystalline lattice in a typical evaluation are also very close: 375 for Cu_2O

and 347 for Ag_2O (ref. 5). Also these oxides possess the properties of semiconductors with the same hole type conductivity (ref. 6). The above comparisons support the contention that Ag_2O has the same diffusion mechanism as Cu_2O , i.e.,

it has the same mechanism for the displacement of metal atoms over the vacancies--over the nodes of the crystalline lattice (ref. 7).

The diffusion mechanism in AgO can be correlated, by analogy, with that in CuO which is close to it. In this case, as in the case of lower oxides of silver and copper, there is a closeness in the chemical properties and in the dimensions of the structural elements. There is also a close analogy in the electrical properties--both oxides are semiconductors with the electron type conductivity (ref. 6, 8).

Thus, on the basis of the above comparisons, we can attribute a diffusion mechanism to AgO which is common to electron semiconductors with an excess of interstitial metallic atoms (of the CuO, ZnO type), where diffusion takes place by the displacement of metallic atoms along the interstices.

Conclusions

1. The contact method in conjunction with the silver-110 isotope has been used to determine the diffusion coefficient of silver in silver peroxide in the temperature range 20 to 85°C and in silver oxide in the temperature range from 20 to 163°C.

2. In the investigated temperature range the diffusion coefficients of silver in silver peroxide varies from 10^{-16} to 10^{-13} $\text{cm}^2 \cdot \text{sec}^{-1}$, while in silver oxide the diffusion coefficient for silver varies from 10^{-12} to 10^{-10} $\text{cm}^2 \cdot \text{sec}^{-1}$.

3. The variation in the diffusion coefficients as a function of temperature is given by the following equations

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$$D = 1.96 \cdot 10^2 \exp(-25600 / RT) \text{ cm}^2 \text{ sec}^{-1},$$

Ag → AgO
20–85° C°

$$D = 5.4 \cdot 10^{-8} \exp(-6960 / RT) \text{ cm}^2 \text{ sec}^{-1}.$$

Ag → Ag₂O
20–165° C

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